PREPARATION AND PROPERTIES OF PURE IRON ALLOYS.

IV. DETERMINATION OF THE CRITICAL RANGES OF PURE IRON-CARBON ALLOYS BY THE THERMOELECTRIC METHOD.

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ABSTRACT.

This paper is an extension of the work by Doctor Burgess and Mr. Scott on the Thermoelectric Measurement of the Critical Ranges of Pure Iron. The apparatus and procedure were practically the same as in the previous work. The material was an exceptionally pure series of iron-carbon alloys prepared by this bureau. This method affords a very accurate means of studying the critical ranges of iron and steel. The results show that the A_2 transformation is constant for heating and cooling up to a concentration of 0.45 per cent carbon and the temperature of the A_3 , A_2 , and A_1 transformations are in agreement with those obtained by other methods.

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I. INTRODUCTION.

In 1916 Burgess and Scott¹ determined the critical temperature ranges of pure iron by means of measurement of the variations in the thermoelectric properties. Because of the lack of careful measurements of the transformations in steels by this method, the further work summarized in this paper was undertaken. Previous to the work of Burgess and Scott many attempts were made to study these critical ranges by the thermoelectric method, but none had much success because of temperature irregularities in furnaces and specimens, lack of pure materials, and the use of long wires of iron or steel, which have the disadvantage of giving the total electromotive force developed between the cold junction, kept at ordinary temperatures, and the hot junction placed in the

¹ Burgess and Scott, Thermoelectric Measurement of the Critical Ranges of Pure Iron, B. S. Sci. Papers, No. 296.

heated region of the furnace. This gives ambiguous results on account of superposition of thermoelectric effects along the iron wire.

The method used by Burgess and Scott was a modification of that used by LeChatelier for measuring thermoelectric power directly, and consisted of using a small specimen of very pure iron in the form of a wire having each of its ends welded to the junction of a platinum-platinum-rhodium thermocouple. The thermocouple gave the temperature at the ends of the wire, while the platinum wires, one from each thermocouple, were used as the leads from the specimen in measuring the emf reading. The method was successful in eliminating difficulties due to uneven temperature gradients. In the present extension of this investigation practically the same method was used, and it was possible to measure the thermoelectric power of steel against platinum for intervals of 2° C. from room temperatures up to $1,150^{\circ}$ C. from observations on the steel wire, which, in each case, was maintained so that the temperature difference between the ends was usually less than 12° C.

II. MATERIAL.

The iron-carbon alloys used in this investigation were made from vacuum fused electrolytic iron melted in an Arsem furnace as described in a paper by Neville and Cain.²

The composition of the material used is shown in Table I.

TABLE 1.—Composition of Material Used.

Specimen number.	Carbon.	Manganese.	Sulphur.	Silicon.
	Per cent.	Per cent.	Per cent.	Per cent.
1.....	0.07	0.54	0.009	0.017
2.....	.31	.05	.004	.005
3.....	.45	nil.	.010	.003
4.....	.54	nil.	.008	.017
5.....	.68	nil.	.009	.002
6.....	1.00	nil.	.005	.004
7.....	1.29	nil.	.010	.006
8.....	1.54		.003	.004

The ingots of metal were annealed and then hot rolled into plates about one-half inch thick. Drillings were made for analysis and a sliver of metal about $\frac{1}{8}$ by $\frac{1}{8}$ by 3 inches was cut as close as possible to the drillings. This sliver was drawn through steel dies to 0.15 cm diameter, and then annealed in a lead bath at 730° C. for one hour. Following the annealing they were cleaned

² Neville and Cain, Preparation and Properties of Pure Iron Alloys, B. S. Sci. Papers, No. 453.

and pickled in 10 per cent H_2SO_4 , after which they were drawn through sapphire dies to 0.08 or 0.05 cm in diameter. The specimens whose carbon content was above 0.68 per cent carbon could not be drawn smaller than 0.08 cm. These wires were then reannealed at 700°C . for one-fourth hour in a lead bath.

III. APPARATUS.

A double-wound platinum-foil resistance furnace of the Hereaus type, 30 cm in length and controlled by the water rheostat described by Burgess and Crowe³ (shown in fig. 1), was used for heating the specimens. In this investigation it was found more convenient to connect the tanks in series both hydraulically and electrically. A 220-volt, 60-cycle current was used for heating the furnace. A White single potentiometer with a Leeds and Northrup high sensitivity galvanometer was used for the emf readings. So as to be able to read the temperature of the ends of the specimen, the temperature difference, and two readings of the thermoelectric power, a special commutator switch was employed to switch the various leads from the thermocouples and the potentiometer separately to the galvanometer. By means of this switch it was also possible to impress a known emf on the galvanometer when desired in order to calibrate the galvanometer scale.

The arrangement of samples in the furnace is as shown in the wiring diagram given below (fig. 2). A length of 1 to 2 cm of the wire specimen was welded (electrically) to the junctions of two platinum-platinum-rhodium thermocouples. This was placed in a quartz tube which was connected to a vacuum pump. The furnace was so constructed that a uniform temperature difference would be maintained along the sample. The furnace had an approximate temperature gradient of 2°C . per 1 cm of length.

IV. PROCEDURE.

Two observers were necessary in taking the readings, one to observe the galvanometer deflections and the other to record the observed values.

The method of taking the readings was as follows: (1) Switch (9) was placed in position *A* and the potentiometer was used to balance the thermoelectric power of the couple. The temperature of one end of the sample was thus obtained.

³ Burgess and Crowe, Critical Ranges A_2 and A_3 of Pure Iron, B. S., Sci. Papers, No. 213 (fig. 6).

FIG. 1.—Water rheostat.

(2) At intervals of 0.02 mv, as indicated by the galvanometer scale, the commutator switch was placed in position *C*, then *D*. This gave two deflections in opposite directions on the galvanometer scale for the thermoelectric power of the iron-platinum couple. The values of these two deflections were averaged, thus balancing out any error due to the shifting of the zero position of the galvanometer.

(3) At intervals of 0.1 mv, as indicated by the potentiometer, the commutator switch was placed in position *B*. This gave the value of the thermoelectric power of the other thermocouple and thereby the temperature of the other end of the wire. The average electromotive force (as determined above) divided by the difference of temperature between the two ends of the wire (1 to 14° C.) was taken as the true thermoelectric power of the iron-platinum couple at the temperature of the hot end of the wire.

The thermocouples and the galvanometer scale were carefully calibrated several times between runs on different specimens. The rate of heating and cooling was approximately the same magnitude throughout, and was about 0.005 mv/sec. (Position *E* on the commutator switch was used for the calibration of scale and galvanometer.)

As a check on the apparatus some wires of pure iron, the same as used by Burgess and Scott, were tried. The composition of this wire was C, 0.009; S, 0.009; P, 0.001; Si, 0.006; Mn, 0.001; and Cu, 0.006.

TABLE 2.—Experimental Results Illustrating the Method Used.

Emf of thermocouple at hot end of specimen (in millivolts).	Temperature of hot end of specimen.	Emf of thermocouple at cooler end of specimen in centimeters of scale deflection. ¹ (1 cm=0.01 mv.)	Emf of steel specimen against platinum in cm of scale deflection.			Thermoelectric power. ¹
			Left.	Right.	Average.	
7.00	° C. 769.5	12.2	3.2	3.2	3.2	0.262
7.02	771.4	-----	3.2	3.2	3.2	.262
7.04	773.2	-----	3.2	3.2	3.2	.262
7.06	775.1	-----	3.2	3.2	3.2	.262
7.08	776.9	-----	3.3	3.1	3.2	.262
7.10	778.8	12.2	3.3	3.1	3.2	.262
7.12	780.6	-----	3.3	3.1	3.2	.262
7.14	782.5	-----	3.2	3.2	3.2	.262
7.16	784.3	-----	3.2	3.2	3.2	.262
7.18	786.2	-----	3.4	3.0	3.2	.262
7.20	788.0	12.2	3.4	3.0	3.2	.262

¹ See explanation below.

Table 2 is a reproduction of part of one of the series of observations which were made while heating a specimen containing 1.54 per cent of carbon. This illustrates the procedure used in recording the observations.

In the above table, the emf of the thermocouple at the cooler end of the specimen is given in centimeters of scale deflection. It should be noted that this value is directly proportional to the temperature, but not equal to it (1 cm approximately equal to 0.95°C.). Likewise, the thermoelectric power as given in the table is not the true thermoelectric power, but is very close to it and directly proportional to it, the corrected value of 0.262 being 0.276.

V. RESULTS.

The results of these experiments are shown by the heating and cooling curves of Figures 3 and 4, respectively. The abscissas are the thermoelectric powers of the steel-platinum couples (see last column in Table 2) and the ordinates are temperatures. Each dot represents an observation in the respective heating or cooling curve. At least four runs were taken on every specimen, a new wire being used each time, so as to be sure that the curve was representative for that material.

It may be noted that the A_2 transformation is identical in its position in all of the curves in which it appears, and that it does not appear in alloys of carbon content higher than 0.45 per cent carbon. According to Honda and Takagi,⁴ who studied the critical ranges by means of the thermomagnetic method, the A_2 transformation does not disappear at a concentration of about 0.45 per cent carbon, but continues completely across the iron-iron-carbide equilibrium diagram. In the present investigation no A_2 transformation could be detected in the steels of higher carbon content.

It will be seen from Figures 3 and 4 that the portion of the curves between A_1 and A_2 transformations and the A_2 and A_3 transformations are of the same slope and would be straight lines except for the break in the vicinity of the A_2 transformation. The portion of the curves above the A_3 transformation and below the A_1 transformation are not extensions of the above portions and are considerably displaced from a straight line that could be drawn along the portion between the A_3 and A_1 transformations.

⁴ Kotaro Honda and Hiroma Takagi, *Die Thermomagnetischen Eigenschaften des Eisen und der Stähle*, Science Reports, Tohoku University, 2, p. 203; 1913.

This may be considered as an indication that the A_1 and A_3 transformations are of a different nature from the A_2 transformation and that the A_2 transformation does not represent a change in the configuration of the internal structure, but suggests an intraatomic change. The conception of intraatomic change was proposed by Honda ⁵ in his theory of ferromagnetism.

This view has been recently confirmed by Westgren ⁶ who, by means of X ray spectrometer methods, showed that the atomic

FIG. 3.—Transformations in iron and steel upon heating, located by thermoelectric measurements.

configuration of iron and steel was without change until the temperature of the A_3 transformation had been exceeded. At this stage the structure changed from a body-centered cube lattice to a face-centered cube lattice; that is, from alpha to gamma iron.

The A_1 and A_3 ranges both occur at lower temperatures as the carbon content increases. No indication of the A_{cm} in the hyper eutectoid steels could be detected by the thermoelectric method. One sample was heated to the melting point. (See fig. 3, curve for 1.54 per cent C.)

⁵ Kotaro Honda, The Nature of the A_2 Transformation, Science Reports of Tohoku University, 4, p. 208; 1915.

⁶ Arne F. Westgren, Röntgen Spectrographic Examination of Iron and Steel, J. Iron and Steel Inst., 103, p. 303; 1921. Also Engineering, 3, pp. 727-728, 757-759; 1921.

It will be noted that by the thermoelectric method, the upper end of the A_3 transformation is sharp. This is not the case when it is determined by other methods. This indicates that in a mixture of two metals of different thermoelectric power, the thermoelectric force which is recorded is that of the metal having the higher power. If this is the case, it would seem that cementite has a greater thermoelectric force than austenite. At the transformation point the thermoelectric force changes abruptly.

FIG. 4.—Transformations in iron and steel upon cooling, located by thermoelectric measurements.

Much trouble was experienced in keeping the wires from decarburizing even in high vacuo. It was found that in some cases, when the heating and cooling series had been taken on the same wire specimen the cooling curve showed no Ar_1 transformation and the Ar_3 was close to 900°C ., thus showing that the wire had been practically entirely decarburized. The very slow heating rate was accountable for the almost complete decarburization of the specimen. It was, therefore, necessary when taking the cooling curve on a specimen, to put in a new piece of wire and heat very rapidly to the temperature from which the cooling was to begin, instead of

using the same wire which had been employed for the heating curve. This difficulty was not experienced to such a great extent in the lower carbon steels.

VI. SUMMARY.

Characteristic curves showing the changes in the thermoelectric properties of pure iron-carbon alloys are given for temperatures up to $1,150^{\circ}\text{C}$. The A_2 transformation was found to be constant at 768°C . for heating and cooling in all alloys having a carbon content up to 0.45 per cent carbon, but it did not appear in alloys of a higher carbon concentration. The characteristics of the curves obtained indicate that the A_2 transformation is of a different nature from the A_1 and A_3 transformations.

The temperatures for the A_3 , A_2 , and A_1 transformations are in fair agreement with those obtained by other methods. The upper end of the transformation is sharp; this is not the case when it is determined by other methods.

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